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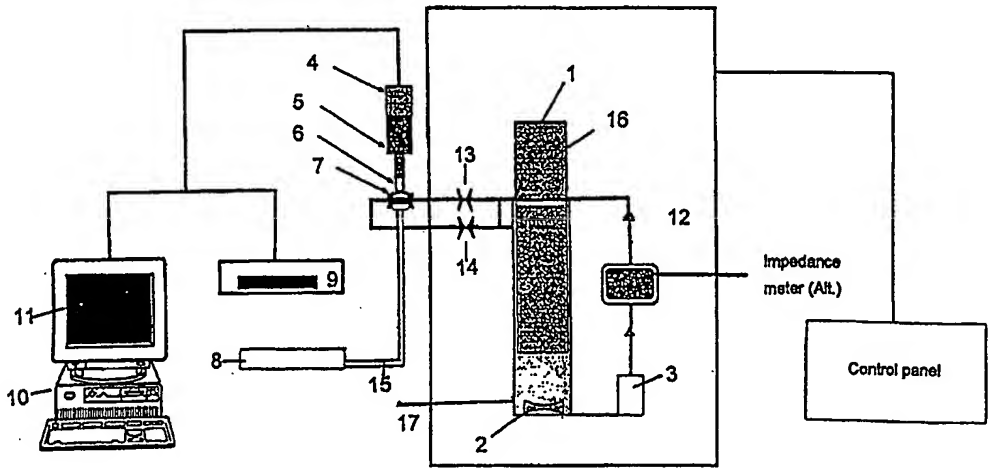
(54) Title: METHOD AND EQUIPMENT FOR THE DETECTION AND ANALYSIS OF THE QUANTITY, ETC. OF PARTICLES IN A LIQUID



(57) Abstract

A method and equipment for the detection and analysis of the quantity of particles which are in or are precipitated in a liquid, for example asphaltenes which are precipitated in oil. The liquid is circulated through a cell (7) which can be trans–illuminated, concentrated, strong light is supplied from a light source (8) to one side of the cell (7) and a digital camera (4), highly magnified (5, 6), takes pictures from the opposite side of the cell. The picture signals from the camera are sent to a data processing unit (10) with a monitor (11) for visual detection and/or further processing of the signals to analyse the particle quantity, etc.

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Method and equipment for the detection and analysis of the quantity, etc. of particles in a liquid

The present invention concerns a method and equipment for the detection and analysis of the quantity of particles which are in or are precipitated in a liquid, for example asphaltenes which are precipitated in oil.

Asphaltenes are defined as the fraction of an oil which is insoluble in N-C_5 and soluble in benzene. In other words, the definition is operational; there is no stringent physical or chemical definition. The asphaltene "monomer" has a varying structure from oil to oil but is generally assumed to consist of aromatic macromolecules which have a significant content of heteroatoms (N, S, O). Asphaltenes are assumed to be present in solution partly as monomers and partly as colloidal aggregates with a continuous size distribution.

It has been demonstrated in experiments that asphaltenes, dissolved in an oil or precipitated, have a very wide size distribution. Typical data show that the molecular weight distribution ranges from approximately 1000 to over 200,000.

Precipitated asphaltenes represent a serious problem in connection with the extraction and processing of petroleum products as they may, for example, be precipitated in the area close to the well and may be deposited in valves, pipes and process equipment. In a worst case scenario, the deposition of asphaltenes in such components and equipment could lead to complete clogging and shutdown with major financial consequences.

Whether asphaltenes will be precipitated in petroleum products, for example crude oil, depends to a great extent on the pressure, temperature and composition of the

oil. Precipitation was expected in few of those cases in which problems have arisen with asphaltene precipitation. This is because the knowledge about asphaltene precipitation is limited and the models used today are only predictive to a certain extent.

Nor is there currently any online equipment for the detection or quantitative analysis of asphaltene precipitation. The equipment which does exist can only be used in laboratories and cannot be used for industrial process control.

A known method uses a source of light in the form of a laser or similar and a light detector, both of which are placed in an oil sample diluted with a solvent. Using an injection device, a flocculant is added to initiate flocculation. The flocculation threshold value (precipitation point) will be detected, using this method, by the light detector registering a reduction in the transmitted light when the flocculation occurs. The method determines only the flocculation threshold value and cannot be used to measure the quantity of asphaltene precipitated. Moreover, it is not selective and consequently will not be able to indicate whether the substances precipitated are actually asphaltenes or other substances, for example sand or wax, which are present in oil.

Another known method for detecting the flocculation threshold value of an oil sample is based on the measurement of the interface tension between oil and water as a function of the quantity of flocculant added. As precipitation takes place, the interface tension increases and the flocculation threshold value can thus be identified. This method cannot be used either to analyse the quantity of precipitated asphaltenes. Moreover, it is uncertain in terms of precision and reproducibility, is labour-intensive and cannot be used in connection with pressure tests.

These last two deficiencies apply also to a third known method, gravimetry, which is based on standard wet chemistry. Oil and a flocculant are mixed in the desired ratio so that asphaltenes are precipitated. The precipitate after precipitation is centrifuged off, washed and weighed. This method is used only to analyse the quantity of

asphaltenes precipitated in an oil sample and cannot demonstrate the flocculation threshold value of the oil without a series of gravimetric analyses which are very laborious and time-consuming.

A fourth method is known from the applicant's own European patent application no. 92203527. This is based on detecting and analysing the quantity of asphaltenes precipitated in crude oil on the basis of measurements of the change in conductivity or capacitance in the oil. The method employs a special measuring cell which provides good, reliable measured results but is relatively expensive to produce and does not either, among other things, offer the opportunity of analysing the size distribution of the asphaltene particles which are precipitated.

The present invention represents a solution which is less expensive than the latter known solution and has further advantages over the prior art. Among other things, the invention offers the opportunity to:

- Visualise the precipitation of asphaltenes under reservoir conditions.
- Analyse the size distribution of the asphaltene particles which are precipitated.
- Estimate the quantity of asphaltenes which are precipitated.
- Analyse the effect of inhibitors on particle size and form.
- Identify whether the precipitation is reversible or irreversible.

The method in accordance with the present invention is characterised in that the liquid which is assumed to contain particles is circulated through a cell which can be transilluminated, concentrated, strong light is supplied from a light source on one side of the cell and a digital camera, highly magnified, recording images from the opposite side of the cell. The image signals from the camera are sent to a data processing unit with a monitor for visual detection and/or further processing of the signals to analyse the particle quantity, etc. as defined in claim 1.

The equipment in accordance with the present invention is further characterised in that it comprises a cell which can be transilluminated and is designed for liquid to flow

through it, a light source which is designed to emit concentrated light to one side of the cell, a camera arranged in connection with the opposite side of the cell with an optical magnification unit between the camera and the cell, which is designed to magnify and record images of the transilluminated, opposite side of the cell, and a data processing unit with a monitor which is designed to receive image signals from the camera and display an image for visual detection and/or further processing of the signals to analyse the particle quantity, etc. as stated in claim 4.

The dependent claims 2 and 3 and 5-9 indicate the advantageous features of the present invention.

The present invention will be described in the following in further detail using examples and with reference to the attached figures where:

Fig. 1 shows an example of a circuit diagram for the equipment in accordance with the present invention.
Figs. 2 a) and b) show an image taken during a test on oil in which asphaltene had been precipitated.
Figs. 3 a) and b) show another image taken during another test on oil in which asphaltene had been precipitated.

Fig. 1 shows, as stated, an example of a circuit diagram for the equipment in accordance with the present invention which comprises an optical detection and measurement unit for asphaltene precipitation in oil. More precisely, the figure shows equipment for use in the laboratory which may expediently also be fitted with a measuring cell to analyse asphaltene precipitation on the basis of measurement of conductivity, which is described in further detail in the applicant's EP patent application no. 92203527 and will not be described in further detail here.

The equipment in accordance with the present invention comprises a mixing cell 1 with an agitator 2 to hold and mix an oil sample to be tested, a circulation pump 3, a digital camera 4 with a compact optical unit 5 and lens 6, a sapphire cell 7, a light

source 8, a video recorder 9 and an electronic data processing unit (PC) 10 with a monitor 11.

The mixing cell 1 (possibly also including a sapphire cell and pipes 12) for the oil sample to be tested for asphaltene precipitation also comprises heating elements (not shown) to keep the oil sample at the desired temperature level. The oil is fed/circulated in a loop from the bottom of the cell 1 through pipes 12 via the pump 3 and the sapphire cell 7 and back to the cell 1. Using valves 13, 14, the flow of oil through the sapphire cell can be adjusted or the sapphire cell can be shut off completely, for example in connection with repairs or replacement of the cell. The pressure in the cell can be adjusted using a piston device 16, which will not be described in further detail here.

The sapphire cell 7 itself comprises a small container with glass of sapphire on two opposite sides so that it is translucent. The distance between the sapphire panes is expediently between 0.2 and 0.4 millimetres. The light source 8 is designed to transmit concentrated light through the sapphire cell via optical cables 15. The digital camera 4 is mounted on the opposite side and is designed to record images (take pictures) of the oil flowing through the cell via the camera's lens 6 and a compact optical unit 7. Together, the lens 6, the optical unit 5 and the monitor 11 produce a total magnification of approximately 1000 x. The camera 4, which expediently has a high resolution (460 lines), transmits signals to the video recorder 9 and PC 10 with the monitor 11.

The video recorder can be used to store the data or pictures taken using the video camera 4 during the measurement/detection of the asphaltene precipitation in the oil. The pictures are then played back and processed using the PC after the measurements have been made. Alternatively, the pictures transferred from the camera 4 can be processed directly by the PC 10.

Very surprisingly, it has been found that it is possible, using the present invention, by transilluminating a sapphire cell with concentrated, strong light and using high

magnification through optical lenses and a video camera, to display a picture of the flowing oil in which any particles of precipitated asphaltenes appear as dark spots or particles (see fig. 2) and which makes it possible to perform data processing to analyse and determine the size and quantity of the particles.

With this equipment, it is therefore possible firstly to visualise the precipitation of asphaltenes, i.e. see when precipitation occurs. Then it is possible, using the PC, to analyse the size distribution of the asphaltene particles and the quantity of asphaltenes which are precipitated. Since the mixing cell is designed to simulate pressures and temperatures (for example 700 bar and 175 ^{o}C) which are present in reservoirs under the surface of the earth, it is also possible to analyse the above values under the prevailing reservoir conditions or the conditions which are present in the process equipment in question on a platform, ship or land.

It is also possible, using the equipment, to analyse the effect of inhibitors on the size and shape of the asphaltene particles and to identify whether the precipitation is reversible or irreversible by manipulating the pressure and temperature in the cell.

Example 1

Oil samples from the Oseberg Øst field in the North Sea were tested. The oil was transferred to the mixing cell and heated up under agitation using the agitator unit 2 and circulated through the pipe loop 12. Then valves 13 and 14 were opened so that the oil could circulate through the sapphire cell 7 and the light source 8, camera 4 and PC with monitor were switched on.

Precipitation of asphaltene was registered at 320 bar and 123^{o}C with the addition of a certain weight fraction of hydrocarbon gas through a supply valve 17. A picture of the registered precipitation is shown in figs. 2 a) and b). More precisely, fig. 2 a) shows the direct picture, while fig. 2 b) shows the same picture converted to black and white using the PC 10.

Example 2

The same test as in example 1 (without the gas) was performed with oil from the Grane field in the North Sea. Precipitation of asphaltene was achieved here by means of pressure relief. The measurements started at 210 bar and the picture shown in figs. 3 a) and b) was taken at 74 bar and 74°C.

Both figures in the above two examples show that it is possible, using the method and the equipment in accordance with the present invention, to take pictures of particles of asphaltenes which are precipitated even in viscous/heavy crude oils.

However, it should be noted that the present invention as it is described in the above is not restricted to the measurement/registration of the precipitation of asphaltenes in oil but can, in reality, be used in all types of liquids in which precipitation takes place or particles are present, for example precipitation of hydrates and wax in oil/gas and particles in emulsions. Moreover, it should be noted that the equipment is not restricted to use in connection with laboratory tests but can be used directly in connection with, for example, process equipment. In such case, the sapphire cell and pipes could be connected directly to the process equipment and fluids could circulate through the cell directly and be examined with regard to the presence of particles.

Furthermore, it should be noted that the present invention is not restricted to the temperatures, pressures or distance between the sapphire panes stated in the above. Nor is the sapphire cell 7 restricted to the use of sapphire glass. The panes in this cell may be made of a material other than sapphire. Moreover, it is possible to use polarised light and special glass in combination to detect wax and other crystalline precipitates.

Claims

1. A method for the detection and analysis of the quantity of particles which are in or are precipitated in a liquid, for example asphaltenes which are precipitated in oil,
characterised in
that the liquid is circulated through a cell (7) which can be transilluminated, concentrated, strong light is supplied from a light source (8) on one side of the cell (7) and a digital camera (4), highly magnified (5, 6), records images from the opposite side of the cell, the image signals from the camera are sent to a data processing unit (10) with a monitor (11) for visual detection and/or further processing of the signals for analysis of the particle quantity, etc.

2. A method in accordance with claim 1,
characterised in
that t the magnification is 1000 x and is produced by using a lens (6) and a compact optical magnification unit (7).

3. A method in accordance with claim 1,
characterised in
that transparent glass of sapphire is used in the cell (7).

4. Equipment for the detection and analysis of the quantity and distribution, etc. of particles which are in a liquid, for example asphaltenes which are precipitated in oil,

characterised in

that it comprises a cell (7) which can be transilluminated and which is designed for the liquid to flow through it, a light source (8) which is designed to emit concentrated light to one side of the cell, a camera (4) arranged in connection with the opposite side of the cell (7) with an optical magnification unit (5, 6) between the camera and the cell, which is designed to magnify and take images of the transilluminated, opposite side of the cell, and a data processing unit (10) with a monitor (11) which is designed to receive picture signals from the camera (4) and display an image for visual detection and/or further processing of the signals to analyse the particle quantity, etc.

5. Equipment in accordance with claim 4,

characterised in

that the optical unit comprises a lens (6) and a compact optical magnification unit (5).

6. Equipment in accordance with claim 4,

characterised in

that a video recorder (9) is arranged in connection with the data processing unit (10) and monitor (11).

7. Equipment in accordance with the preceding claims 4-6, characterised in that it is designed for use for in situ measurements in process plants or similar, where the sapphire cell (7) is supplied with liquid via pipes (not shown) directly from the pipelines or process equipment of the process plant.

8. Equipment in accordance with the preceding claims 4-6, characterised in that it is designed for use in laboratories, where the sapphire cell is supplied with liquid via pipes (12) from a mixing cell (1).

9. Equipment in accordance with claim 8, characterised in that the mixing cell (1) is equipped with an agitator (2).

10. Equipment in accordance with claim 8, characterised in that the mixing cell is provided with a piston unit (16) for pressure regulation.

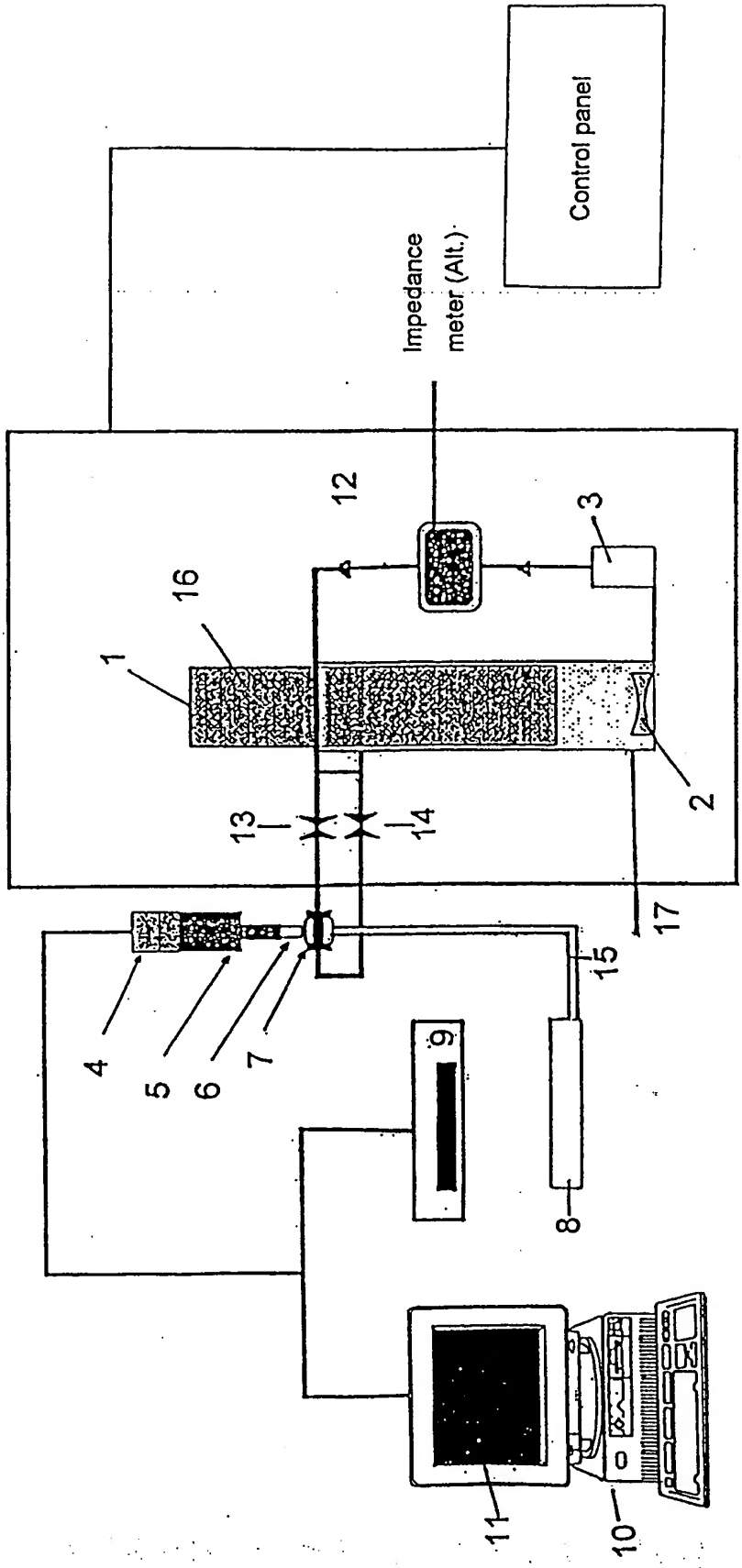
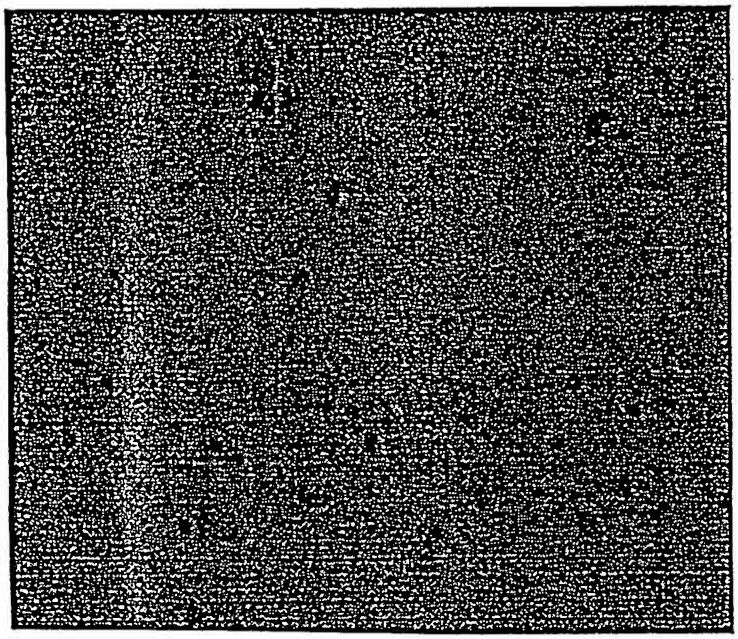

Control panel
Impedance meter (Alt.)
12
3
16
1
2
13
14
17
15
4
5
6
7
9
8
11
10

Fig. 1

Fig. 2

a)



b)

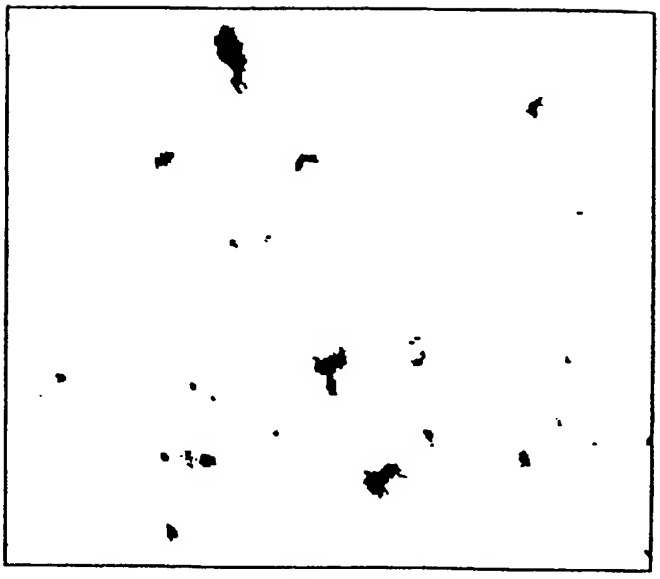
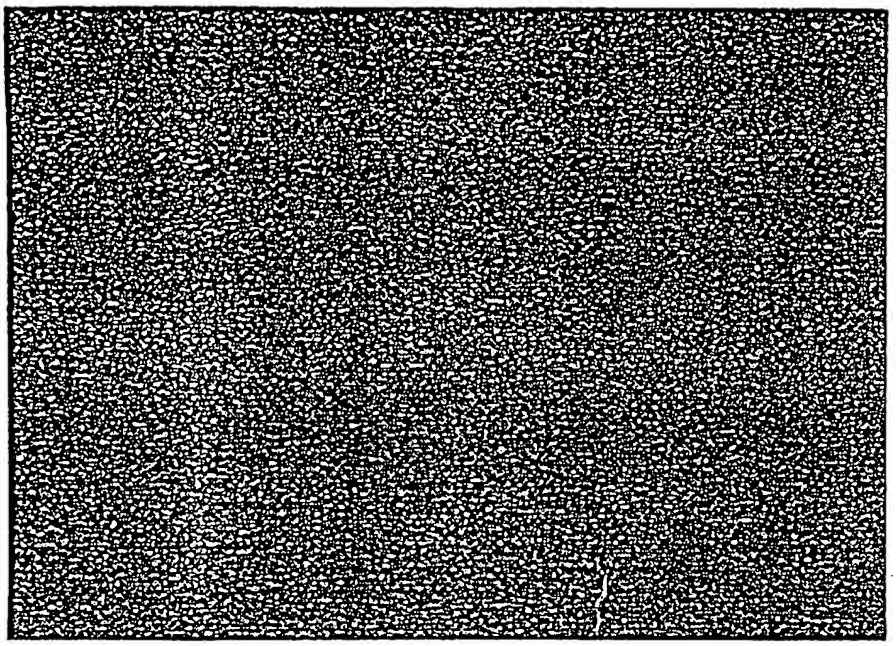
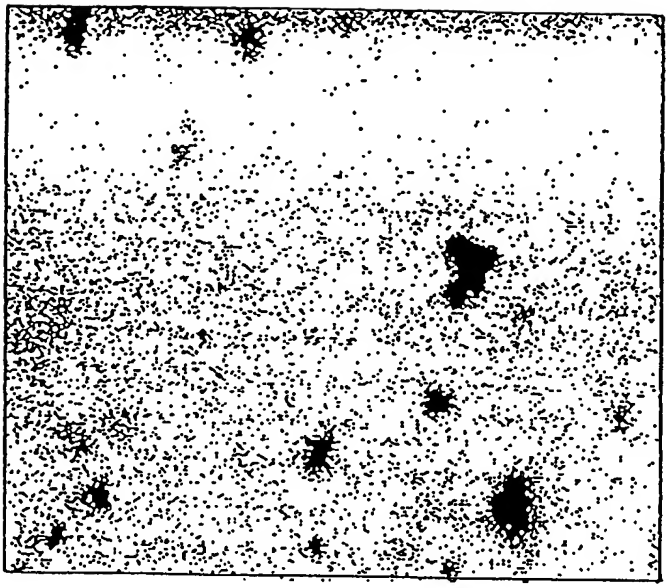


Fig. 3

a)



b)



INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00110

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 15/00, G01N 21/05, G01N 33/28
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI,EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0791816 A2 (HITACHI, LTD.), 27 August 1997 (27.08.97), page 2, line 35 - line 58; page 7, line 5 - line 22; page 9, line 7 - line 26, figure 1 --	1-10
X	US 5521699 A (TOKIHIRO KOSAKA ET AL), 28 May 1996 (28.05.96), column 2, line 55 - column 3, line 15; column 5, line 7 - line 16, figures 1,6,11 --	1-10
X	EP 0543514 A2 (TOA MEDICAL ELECTRONICS CO., LTD.), 26 May 1993 (26.05.93), column 4, line 37 - line 58; column 5, line 31 - column 6, line 50, figure 2, abstract --	1-10

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 1999	13 -07- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Marianne Bratsberg/MP Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00110

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E,X	DE 19744246 A1 (SUHR, HAJO), 29 April 1999 (29.04.99), figure 1	1-10
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A	EP 0245512 A1 (COSMO OIL COMPANY, LTD.), 19 November 1987 (19.11.87)	1-10
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A	US 5770795 A (EMMANUEL BEHAR ET AL), 23 June 1998 (23.06.98)	1-10
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO99/00110

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Invention 1: claims 2 and 5

Invention 2: claim 3

Invention 3: claim 6

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/06/99

International application No.
PCT/NO 99/00110

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